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Electron spin resonance linewidths of Co^{2+} in magnesium oxide

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Electron spin resonance linewidths of Co^{2+} in single-crystal MgO at 9 GHz were examined experimentally and theoretically for a range of Co^{2+} concentration from 310 to 9900 ppm. In contrast to the behaviour expected from dipolar broadening, the experimental peak-to-peak linewidth for the octed hyperfine lines were about twelve to fifty times less than the calculated dipolar linewidths according to temperature and concentrations. The peak-to-peak linewidths as determined experimentally increase from 0.8 mT at 310 ppm Co^{2+} to 4.0 mT at 9900 ppm Co^{2+} at a polar angle $\theta_H = 0°$ and at 20 K. Peak-to-peak linewidths independent of polar angle but strongly dependent on temperature and slightly dependent on concentrations were observed. The ratio of moments $M_4^{1/4}/M_2^{1/2}$ derived from the experimental data lay between 1.35 to 1.44 and the lineshapes were markedly Lorentzian in the range of temperature measured. The data suggest that Co^{2+} entered the lattice substitutionally, occupying magnesium sites, that the linewidths were determined, after exchange energy, over the whole concentration range examined and that the exchange energy whose values lay between 6 and 77 GHz, varied linearly with concentration.

1. Introduction

The electron spin resonance (esr) linewidth results of Fe^{3+} and Cr^{3+} in magnesium oxide showing exchange interactions have recently been reported [1, 2]. As part of further studies on different ions, a similar investigation has been made of the cobalt-doped magnesia (Co^{2+}/MgO) in an attempt to provide specimens of known structural characteristics on which electrical conductivity and dielectric loss measurements might subsequently be made. The esr spectra of Co^{2+}/MgO was first observed by Low in 1958 [3] and then by Fry and Llewellyn in 1962 [4], where the characteristic parameters of the spin-Hamiltonian were calculated for cubic crystalline field. There is, however, little detailed information available either on the question of the sites actually occupied by the dopant atoms or on the nature of the interactions between the latter. Information of this nature has been obtained in the literature [1, 2], by making a comparison between observed esr linewidths and those predicted from dipolar broadening. It was decided to adopt a similar approach with Co^{2+}/MgO. The divalent ion of cobalt has electronic configuration of $3d^7(^4F_{9/2})$. In the MgO lattice the ^4F level splits into three, and these are further split by spin orbit interaction [3] and the lowest level is a Kramers doublet. Since the only natural isotope of cobalt is ^{59}Co, which has a nuclear spin $I = 7/2$, considerable hyperfine interaction is expected. This paper presents the results of the linewidth comparison made for the hyperfine transitions in the ground doublet of Co^{2+}.

2. Experimental techniques

The doped single crystals on which measurements were made were obtained from W. & C. Spicer Ltd (Cheltenham), having been grown by electrofusion using pure powdered cobalt oxide and pure powdered magnesia as starting materials. The cobalt concentrations in the specimens examined ranged from 310 to 9900 ppm, these have been

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determined by optical spectrographic analysis (Johnson-Matthey Ltd) to an accuracy of about 2%. The crystalline quality was good and neither optical examination nor X-ray back-reflection photographs, used to orient the specimens, revealed any evidence of macroscopic cracking, flaws, strain or mosaic formation. This led us to assume that the samples were of good crystalline quality. The crystals were coloured varying from very light pink at 310 ppm Co to deep pink at 9900 ppm Co.

The esr measurements were made both using a conventional 9 GHz spectrometer [2] and a X-band commercial Varian spectrometer. Since the spectrum of Co^{2+}/MgO is only visible below about 65 K, the spectrometers were equipped with helium cryostats having temperature control devices. Spectra were recorded in the range 4.2 to 65 K, by sweeping the magnetic field slowly through a known range. The magnetic field calibrations were obtained using a proton resonance magnetometer system in which the probe could be located exactly in the position normally occupied by the specimen.

3. Experimental results

Initial measurements were made to establish the form of the spectrum in each specimen at various temperatures. An example of this is shown in Fig. 1, which refers to a specimen containing 310 ppm Co examined at temperatures between 4.2 and 65 K. The spectrum, which is isotropic, shows a total of eight hyperfine line with g value about 4.278 and with hyperfine constant about $A = 98.0 \times 10^{-4}\ \text{cm}^{-1}$. The values at which the transitions occurred when compared with the values expected from the energy level diagram [5]. There was close agreement and on this basis, and in view of the similarity between Fig. 1 and the features of the liquid helium temperature spectra reported for the 1 and 3 cm regions, respectively, in [3] and [6], it was felt justifiable to attribute the spectrum to Co^{2+} in the octahedral sites. A conspicuous difference in the intensity and the hyperfine line energy separation A was observed between the low and high magnetic field sides. Even at high gain the crystals showed only the lines due to Co^{2+} and a weak line due to iron, which suggests that these crystals are of higher degree of perfection than the corresponding Cr^{3+}/MgO sample [2]. This is possibly due to the fact that since the Co^{2+} ion is doubly charged, a direct substitution for Mg^{2+} is possible in the MgO lattice without the need for charge compensating vacancies.

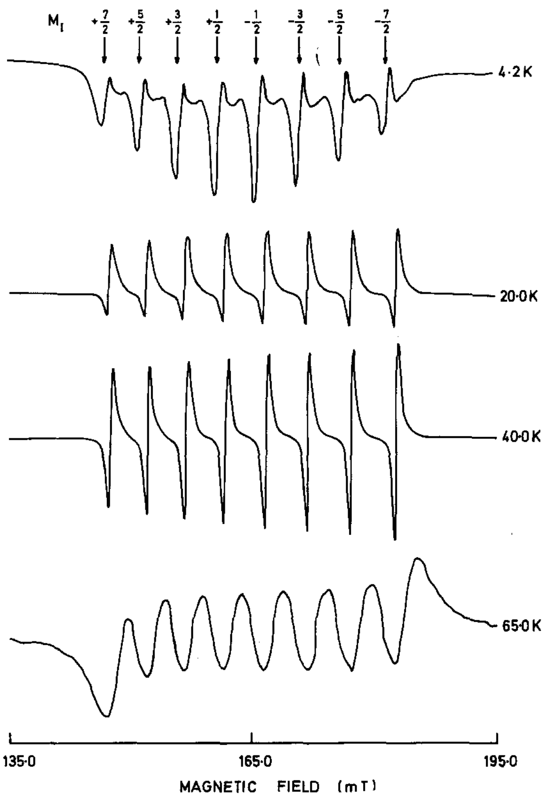

Figure 1 Variation of lineshape with temperature. Co^{2+}/MgO (310 ppm) 9.515 GHz, $\theta_H = 0°$.

The linewidth determinations were made at $\theta_H = 0°$. The linewidths of the eight hyperfine lines were equal to each other and were independent of polar angle θ_H, but strongly dependent on temperature (Fig. 2). There is some difficulty

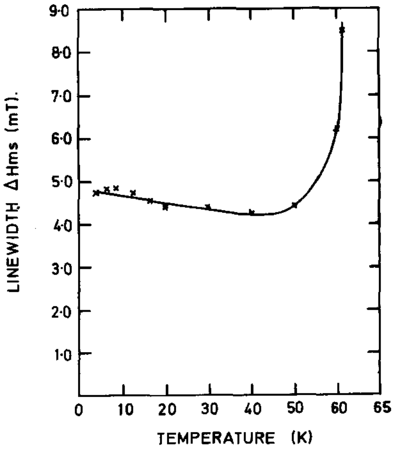

Figure 2 The temperature dependence of the linewidth for Co^{2+}/MgO (8200 ppm), 9.515 GHz, $\theta_H = 0°$.

in ascertaining the linewidth at high temperatures and, above 50 K, the points marked on Fig. 2 have been derived from the separation of points of inflection on the derivative plots. The linewidths were also slightly dependent on concentration but not by as much as the $(\text{concentration})^{1/2}$ behaviour expected from dipolar theory. Increases in resonance linewidth for higher dopant concentrations have been reported by Fry and Llewellyn [4] in the endor experiments. There was no change in either the resonance field or the hyperfine constant A with polar angle at temperatures in the range measured. The peak-to-peak linewidth, defined as the width between points of maximum slope, ΔHms, was obtained directly from the derivative plots. As the temperature decreased from 65 K the linewidth first decreased to a minimum at about 40 K and then increased from 20 K down to 4.2 K. For all the specimens, the linewidths ΔHms at 4.2 K were less than the linewidths at 60 K. For the low concentration specimen (310 ppm Co) at temperatures of 20, 4.2 and 60 K, the linewidths ΔHms were 0.8, 1.7 and 2.4 mT, respectively, while for the high concentration specimen (9900 ppm Co) the values of ΔHms for the corresponding temperatures were 4, 4.9 and 4.9 mT, respectively.

4. Dipolar broadening

It will be assumed in this calculation that the main contribution to homogeneous line broadening is dipole–dipole interaction between Co^{2+} ions. The second moment $\langle\Delta\omega^2\rangle$ of the linewidth caused by dipolar interaction between identical atoms in the magnesium oxide lattice has been derived in the literature [1]. For Co^{2+}, $S = \frac{3}{2}$ and $g = 4.278$ [3] and so the atomic part of the second moment is $6.2644 \times 10^{-24}\, n$ $(\text{rad sec}^{-1})^2\ \text{cm}^6$, which leads to the final equation for second moment

$$\langle\Delta\omega^2\rangle = 6.2644 \times 10^{21}\, n \times [15.9184 - 5.175 Y^*_{4,0}(\theta_H, \phi_H) - 6.218 Y^*_{4,4}(\theta_H, \phi_H)], \quad (1)$$

where the symbols have their usual meanings as described in [1]. Using the transformation equation and considering $\phi_H = 0°$, the peak-to-peak derivative linewidths ΔHms can be evaluated and compared with experimental values. The general curves for the variation of linewidth with polar angle are given in Fig. 3, which also shows the experimental values of linewidth. The predicted concentration dependence of linewidth at $\theta_H = 0°$ (obtained from Fig. 3) is shown in Fig. 4, which also gives the experimental points.

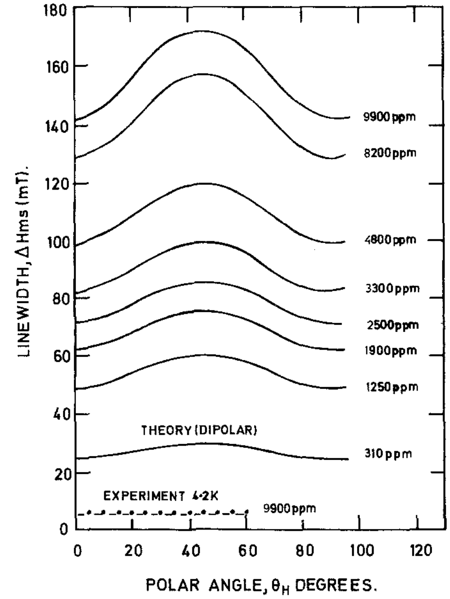

Figure 3 Comparison of predicted and observed variation of linewidth with polar angle.

5. Discussion

Two salient features emerge from initial comparison between the experimental results for the as-grown crystals and dipolar theory. Firstly, the predicted linewidths are about fifty times larger than the observed linewidths; secondly, the linewidth appears to be independent of polar angle in contrast to the maximum linewidth at 45° expected for dipolar broadening. The former discrepancy was similar to that encountered with both Fe^{3+}/MgO [1] and Cr^{3+}/MgO [2]. These both showed linewidths of about 100 times less than the predicted dipolar widths, an effect attributed to exchange narrowing; the independence of width on polar angle has also been observed in Cr^{3+}/MgO. In Co^{2+}/MgO, the measured linewidth varied from between twelve and fifty times less than predicted by dipolar broadening theory (Table I). This large numerical disparity in Co^{2+}/MgO suggested that there was a strong narrowing mechanism such as had previously been found in both Fe^{3+}/MgO and Cr^{3+}/MgO.

To substantiate the possibility of exchange narrowing within the range of measured concentrations and temperature, additional evidence based on lineshape analysis has been obtained and

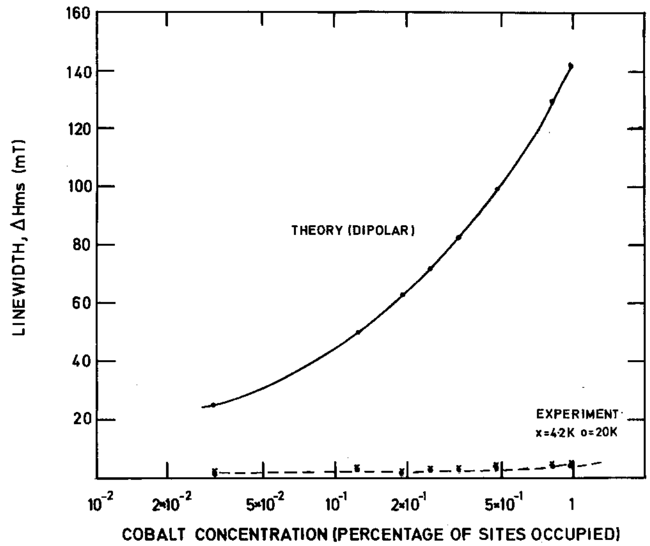

Figure 4 Comparison of predicted and observed variation of linewidth with concentration; $\theta_H = 0°$, 9.51 GHz.

these data are also given in Table I. To obtain the data it was considered that in all cases an undistorted lineshape could be obtained from the leading (or trailing) half of the first (or last) line of the octet; this, when integrated, gave one side of the absorption line. It was also assumed that the line was symmetrical about the mid point. The ratio $M_4^{1/4}/M_2^{1/2}$ (where M_2 and M_4 are, respectively, the second and fourth moments) was then derived and the results are tabulated in column 5 of Table I. The values of the ratio are similar to the figures quoted for Fe^{3+}/MgO [1] and Cr^{3+}/MgO [2]. This suggests that at temperatures between 60 and 4.2 K exchange narrowing is important, even at the lowest cobalt concentration (310 ppm).

The lineshape factor is defined as the ratio of the peak-to-peak derivative linewidth, ΔHms, to the width of half-height, $\Delta H_{1/2}$, of the absorption curve. The values of this factor for Lorentzian and Gaussian lines are, respectively, 0.577 and 0.846

TABLE I Lineshape data for a range of cobalt concentrations at temperatures of 4.2, 20 and 60 K; 9.515 GHz, $\theta_H = 0°$

(1) Cobalt concentration (ppm)	(2) ΔHms (dipolar) $\theta_H = 45°$ (mT)	(3) Temperature (K)	(4) ΔHms (obs) (mT)	(5) $\dfrac{M_4^{1/4}}{M_2^{1/2}}$	(6) $\dfrac{\Delta Hms\text{ (obs)}}{\Delta H_{1/2}\text{ (obs)}}$
310	30.1	4.2	1.7	1.44	0.57
		20	0.8	1.39	0.57
		60	2.4	1.396	0.61
1250	60.1	4.2	2.9	1.358	0.58
		20	2.1	1.41	0.55
2500	86.7	4.2	2.9	1.365	0.48
		20	2.1	1.41	0.64
3300	99.7	4.2	2.9	1.39	0.47
		20	2.0	1.39	0.51
4800	120.1	4.2	3.6	1.36	0.50
		20	2.4	1.38	0.57
		60	3.9	1.37	0.55
8200	157.1	4.2	4.7	1.37	0.69
		20	4.4	1.43	0.65
		60	6.3	1.41	0.58
9900	172.6	4.2	4.9	1.35	0.63
		20	4.0	1.37	0.54
		60	4.9	1.39	0.67

TABLE II Evaluation of exchange energy and Weiss constant, for various concentrations of cobalt, 4.2 K

Sample concentration (ppm)	Exchange energy (GHz)	Weiss constant θ (K)
310	6.11	0.88
1250	14.67	2.10
2500	25.48	3.66
3300	33.00	4.75
4800	40.76	5.87
8200	7374	10.61
9900	77.60	11.17

[7]. Exchange narrowing would make the line adopt a Lorentzian shape. To confirm this, the widths at half-height, $\Delta H_{1/2}$, have been calculated from the observed integrated lineshapes and the ratio of $\Delta Hms/\Delta H_{1/2}$ derived; the values are tabulated in column 6 of Table I and show that the lineshapes are more Lorentzian than Gaussian in the range of concentration and temperature used.

The assumption, on the above basis, of an exchange-narrowed model enables evaluation of the exchange energy J to be made by adopting the method used previously [2]. The values of J for the different specimens at 4.2 K have been tabulated in column 2 of Table II. Further, a plot of J against concentration gives a straight line as shown in Fig. 5. If this line is extrapolated to 50% of the available sites occupied by Co^{2+}, i.e. to the point corresponding to CoO, an exchange energy of 32×10^{11} Hz is obtained. This may be compared with the value for CoO of 1.43×10^{11} Hz obtained from the temperature dependence of susceptibility [8] and also with the reported value of $J = 6.298 \times 10^{11}$ Hz as measured from the intensity of pair spectra in Co^{2+}/MgO [9].

We have also calculated the values of Weiss constant θ, from the Weiss molecular field equation

$$3k\theta = 2JzS(S+1) \tag{2}$$

where z is the number of nearest neighbours and k is the Boltzmann constant; in the MgO lattice $z = 6$.

Even though the actual spin of Co^{2+} is $\frac{3}{2}$, we observed only the octet of hyperfine lines due to the interaction between an effective spin of $\frac{1}{2}$ and the nuclear spin $I = \frac{7}{2}$. Thus taking $S = \frac{1}{2}$, the values of θ have been evaluated from Equation 2 and tabulated in column 3 of Table II. Similar effective spin value considerations have been reported in the literature [9, 10]. A plot of θ against concentration also gives a straight line (Fig. 5). If this line is extrapolated to the point representing pure CoO, a value of Weiss constant $\theta = 550$ K is obtained. This is comparable to the literature value CoO of 330 K [11] and thus supports the validity of assuming $S = \frac{1}{2}$.

The differences in both the intensity and hyperfine energy separation A in the octet spectrum of Co^{2+}/MgO are the same at all temperatures. These effects may be due to cross-relaxation between cobalt ions, an interaction which also is temperature independent. Cross-relaxation would be expected to affect the population distribution in the components of the octet and hence their relative intensities. Cross-relaxation between cobalt ion in MgO has been reported by Pryce [5] for specimens containing less than 230 ppm Co and so cross-relaxation would be very likely at the higher doping levels used in the present work. The increase of linewidth, ΔHms, in the range of temperature 20 to 4.2 K may be due to unresolved hyperfine interaction with the ^{25}Mg nuclide while the increase in linewidth above 40 K can be attributed to relaxation broadening.

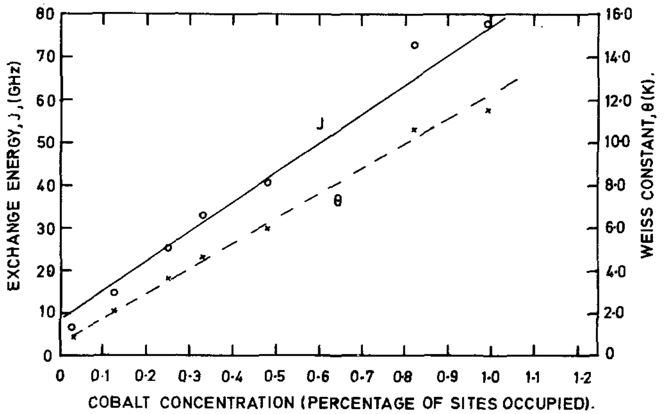

Figure 5 The variation of J and θ with cobalt concentration, 4.2 K.

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